

PHASE RELATIONSHIPS IN FLUORINE-BEARING LADLE SLAGS

C. Reinke and J. Nell

Mineralogy Division, Mintek
Private Bag X3015
Randburg 2125
South Africa

e-mail: ChristianR@Mintek.co.za
JohanN@Mintek.co.za

Abstract We investigated phase relationships in slags containing about 54 wt% CaO, 20 wt% Al₂O₃, 6 wt% MgO, and 0–14 wt% CaF₂, balanced by SiO₂. Fluorine losses present a considerable experimental challenge when moisture, even in trace amounts are present in the samples. From a combination of thermal analysis measurements and quench experiments we bracketed the liquidus temperature of slags containing between 3 and 10 wt% CaF₂ to be between 1400 °C and 1550 °C. The liquidus temperature of slag containing more fluorine (14 wt % CaF₂) is above 1550 °C. The primary liquidus phase in slag containing less than 11 wt% CaF₂ is MgO – slags containing more CaF₂ have CaO on the liquidus. The amount of monoxide that forms is small and the main “melting event” (which controls the fluidity of the slag) is controlled by the melting of Ca₃SiO₅ and Ca₁₂Al₁₄O₃₂F₂. This takes place at temperatures between 1250 °C and 1370 °C. Our observations are consistent with formation of Al-F melt complexes, similar to what has been found in more silica-rich liquids.

1. INTRODUCTION

Fluorine-bearing slags are commonly used in steelmaking yet much remains unclear about phase-relationships in $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-CaF}_2$ slags at elevated temperatures. Liquidus phase diagrams are available for the $\text{CaO-SiO}_2\text{-CaF}_2$, $\text{CaF}_2\text{-MgO-SiO}_2$, $\text{CaF}_2\text{-CaO-MgO}$, $\text{Al}_2\text{O}_3\text{-CaF}_2\text{-CaO}$, $\text{Al}_2\text{O}_3\text{-CaF}_2\text{-SiO}_2$, $\text{Al}_2\text{O}_3\text{-MgO-CaO-CaF}_2$ and $\text{Al}_2\text{O}_3\text{-CaO-MgO-Al}_2\text{O}_3$ sub-systems (see the compilation of phase diagrams in [1]) but when five-component slags are encountered it is not immediately evident from these diagrams what the liquidus temperatures are, or what the sequences of phases are that crystallise during cooling. We have also found that commercial thermodynamic modelling software do not adequately deal with ladle slags from a typical stainless steel operation. These deficiencies prompted an experimental study to investigate melting behaviour (liquidus temperature and cooling path) of synthetic ladle fluxes containing different ratios of SiO_2 -to- CaF_2 .

Synthetic slags containing about 54 wt% CaO , 20 wt% Al_2O_3 , 6 wt% MgO , and 0–14 wt% CaF_2 , balanced by SiO_2 , were studied. The experimental strategy can be summarised as follows:

- For each composition we determine the temperature range over which most of the slag melts. (The main melting event as observed by differential thermal analysis does not necessarily correspond to the liquidus temperature. Small amounts of crystalline phases are frequently present in the slag above the main melting temperature.)
- At temperatures above and below the main melting temperature, we identify the solid phases that are present using powder X-ray diffractometry (XRD) and reflecting light microscopy.
- In samples quenched from selected temperatures above and below the main melting event, we determine the compositions of the solid phases and quenched glass using electron probe microanalysis (the cation and fluorine concentrations were determined by wavelength dispersive spectrometry).

The experiments allow us to bracket the liquidus temperatures of slags with different SiO_2 -to- CaF_2 ratios and provide information on the phase-chemistry of the slags between their liquidus- and solidus-temperatures. With this information it is possible to take a view on the optimum CaF_2 addition to the ladle taking into account compatibility with the refractories and the negative environmental impact of slags containing excessive concentrations of fluorine.

2. EXPERIMENTAL PROCEDURES

Considerable experimental problems related to fluorine losses were experienced during the execution of the project. Fluorine losses are attributed to the formation of HF during reaction. The slags are saturated with CaO (lime), MgO (periclase) or $(\text{Ca,Mg})\text{O}$ solid solutions. Hydration of these phases is practically inevitable even when the samples are stored in an evacuated desiccator. To avoid the introduction of hydrogen in the experiments, careful sample preparation was required. It also necessitated the use of infrared spectroscopy (IR) to monitor the moisture content of samples and thermogravimetry (TG) to assure that fluorine

losses were not incurred during reaction. Bulk chemical analysis served as a final check on the preservation of fluorine during experimentation.

Experiments were conducted under different conditions in open systems, where the flux is exposed to a flowing gas, as well as in closed systems with the material sealed in quartz glass or platinum ampoules. In an attempt to overcome the experimental problems that were encountered, different procedures were followed in the preparation of the starting materials and in executing the experiments. Details on experimental procedures would normally not be included in a manuscript of this nature but because technique development formed an important part of work we have decided to deviate from the norm by providing this information in Appendix 1.

Samples are designated by their *nominal* CaF₂ content, appended by an “a” when CaF₂ was added immediately before an experiment. For instance, “flux 6” refers to the material with 6 wt% CaF₂ and 14 wt% SiO₂. “Flux 6a” refers to material with the same bulk composition (6 wt% CaF₂), but in this instance the flux components were not homogenised through a pre-reaction anneal.

3. RESULTS AND DISCUSSION

3.1 Bulk Chemistry

The bulk chemical composition of the fluxes is given in Table 1 (compositions were determined by Mintek’s Analytical Science Division and by an independent laboratory using emission spectroscopy for cations and wet-chemical methods for the fluoride content). In relative terms the measured CaF₂ concentrations differ by as much as 50 per cent from the nominal values (e.g., flux 2). We suspect that the discrepancy is partly due to difficulties in the analytical measurement of fluorine. More than anything else bulk chemical analysis confirms that the fluxes did not suffer extensive fluorine losses during preparation. The fluxes can be used with confidence for further experimentation.

3.2 Mass Loss on Heating

The thermogravimetric data show that mass loss takes place in two steps (Figure 1). The main mass-loss event spans the temperature range between about 400 °C and 800 °C (4 wt%). Further heating to 1630 °C is associated with a further mass loss of about 0.3 wt%. We expect three types of reactions are responsible for mass loss in this system (besides the trivial case of water being adsorbed at the surface):

- Reaction with humidity, e.g., $\text{CaF}_{2(\text{slag})} + \text{H}_2\text{O} = \text{CaO}_{(\text{slag})} + 2 \text{HF}_{(\text{gas})}$. (1)
- Dehydroxylation, i.e., reactions of the type $\text{Ca}(\text{OH})_{2(\text{slag})} = \text{CaO}_{(\text{slag})} + \text{H}_2\text{O}_{(\text{gas})}$. (2)
- Evaporation of volatile slag components, e.g., CaF₂, SiF₄, or AlF₃, possibly catalysed by humidity [2]. (3)

The mass loss below 800 °C is suspected to be due to dehydroxylation. The evidence is as follows:

- The relatively high temperature of the event. Surface moisture is typically removed at lower temperatures (<150 °C).
- An endothermic flow of heat is associated with the TG step below 800 °C. This is characteristic of dehydroxylation reactions such as Reaction (2).
- IR spectroscopy shows that the unreacted flux contains crystalline O-H bonds (characterised by a peak at about 3640 cm⁻¹) – such bonds are not detected in the flux after heating to 800 °C (Figure 2). The O-H bond peak, however, re-appears after the reacted sample has been stored for some time.
- Chemical analysis confirms that the low-temperature mass loss is not accompanied by the loss of fluorine (e.g., data for flux 6, Table 1).

Continuous high-temperature mass loss is probably due to evaporation of slag components (Reaction (3)) and reactions with traces of humidity in the gas (Reaction (1)).

Samples reacted in platinum loops experienced massive fluorine losses (Figure 3), probably according to Reactions (1) and (3). The CaF₂ content of flux 12, for example, decreases by about an order of magnitude after 15 hours in air at about 1500 °C. The high-temperature mass loss of samples suspended in Pt loops is much larger than that of samples reacted in Pt crucibles in argon (Figure 1). This is probably due to the smaller surface-to-volume ratio in crucibles as well as differences in gas humidity, air being more humid than argon (bearing in mind that fluorine losses are largely due to the formation of HF).

3.3 Section of a Phase Diagram for the System Al₂O₃-CaF₂-CaO-MgO-SiO₂

3.3.1 Information from Thermal Analysis

For each flux we determined the temperature range of the main melting event by thermal analysis. Data were collected during heating and cooling. The slags containing CaF₂ display similar DTA patterns on heating (Figure 4). The trace for flux 0 (that does not contain CaF₂) displays thermal events that are not present in the fluorine-bearing fluxes. The phase chemistry of flux 0 was not investigated further, but it is important to note that the addition of fluorine, even in small amounts (3 wt% CaF₂), makes a considerable difference to the melting behaviour of the slag.

Cooling patterns differ from heating patterns, and not all the samples display the same features. Data collected during cooling were largely neglected due to supercooling and because peaks at high temperature were very broad.

From Figure 4 we identified the main melting event for each slag. For flux 12 the top of the main melting peak is at 1312 °C. The peak is broad and asymmetric, spanning from about 1250 °C to 1330 °C. The broad, asymmetric shape of the peak is consistent with an incongruent melting event. In fluxes containing less CaF₂, the main melting peak shifts to higher temperatures (1374 °C in flux 2), and it becomes narrower and more symmetric. Peak

shapes and widths of thermal events at lower temperature also tend to vary between samples, but their position is, in general, less dependent on the CaF_2 content of the flux.

Figure 5 shows a summary of thermal events above 1150 °C (recorded during heating). The two lines at the top represent the onset and top, respectively, of the main melting peak. The nature of the thermal event at about 1150 °C has not been determined.

The line from 1312 to 1374 °C represents the *main melting event* for the fluorine-bearing slags. Note that this is *not* the liquidus line. Quench experiments (see below) show that some crystalline phases are present in fluxes quenched from temperatures above the main melting line. The thermal analyser does not detect the melting of these phases at higher temperature during heating.

3.3.2 Information from Quench Experiments

Following the thermal analysis experiments, we conducted quench experiments on selected fluxes from different temperatures to obtain information on their phase chemistry at temperatures between the liquidus and solidus. Table 2 lists the phases that were identified in quenched samples. Electron microprobe analyses of the crystalline phases and quenched glass and their estimated amounts are given in Table 3. We note the following:

- At 1450 °C and 1550 °C ladle fluxes containing between 6 and 12 wt% CaF_2 (fluxes 6 to 10) are fully molten (Ca_3SiO_5 in flux 6a quenched from 1450 °C may have formed during cooling). Flux 12, however, is saturated with CaO even at 1550 °C.
- At 1400 °C fluxes 6–10 contain glass and crystalline phases; i.e., the *liquidus temperatures* of these fluxes are between 1400 °C and 1550 °C. The liquidus temperature of flux 12 is above 1550 °C.
- The temperature spacing of the quench experiments is not small enough to permit the unambiguous identification of the primary liquidus phase. The absence of silicate phases in flux 12 quenched from 1550 °C and in flux 10 quenched from 1400 °C suggest that a monoxide phase (CaO or MgO) first crystallises from the liquid during cooling under equilibrium conditions. Our data indicate that MgO crystallises in slags containing less than 11 wt% CaF_2 and that both MgO and CaO are present when the flux contains more CaF_2 . Noting that the SiO_2 content of fluxes 6 to 12 is below 15 wt%, the initial crystallisation of monoxides would be in qualitative agreement with the large primary liquidus fields of monoxide phases (CaO and MgO) in simple three-component phase diagrams (e.g., CaO-MgO- SiO_2) at low SiO_2 levels.
- It is not clear if Ca_2SiO_4 forms under equilibrium crystallisation conditions. It was observed in two compositions quenched from 1400 °C, but not at lower temperatures. To the extent that three-component phase diagrams such as for the system CaO-MgO- SiO_2 can be used to model the cooling behaviour of the more complex ladle slags, we expect that Ca_3SiO_5 would follow the crystallisation of monoxide phases. When the data at 1350 °C are considered this, indeed, seems to be the case. We suspect that the presence of Ca_2SiO_4 in some samples is a quench phenomenon.
- Fluxes 6a and 10a quenched from about 1360 °C contain significant quantities of Ca_3SiO_5 in addition to monoxides (MgO in flux 6a and both CaO and MgO in flux 10a).

In samples quenched from 1225 °C, we observe the crystallisation of $\text{Ca}_{12}\text{Al}_{14}\text{F}_2\text{O}_{32}$ and a significant increase in the amount of Ca_3SiO_5 (Table 3). The fluxes are essentially solidified at 1225 °C; i.e., the thermal event between about 1250 and 1370 °C (Figure 5) is, indeed, due to melting.

- Ca_3SiO_5 invariably contains small amounts of fluorine in solid solution (a typical composition is $\text{Ca}_{2.84}\text{Mg}_{0.14}\text{Al}_{0.15}\text{Si}_{0.90}\text{O}_5 \cdot 0.073\text{CaF}_2$). The practical implication of this is an expansion of the liquidus stability field of Ca_3SiO_5 in fluorine-bearing systems.

That $\text{Ca}_{12}\text{Al}_{14}\text{F}_2\text{O}_{32}$ (and Ca_3SiO_5) are the final phases to crystallise from the fractionated slag is consistent with the increase in the concentration of alumina and, to a lesser extent, also fluorine in the melt during cooling (Figures 6 and 7; see glass analyses in Table 3). The increase in the concentration of alumina is due to the fact that none of the phases that initially crystallise from the slag (e.g., CaO , MgO , and Ca_3SiO_5) contain Al_2O_3 in their structures. The CaF_2 content of the fractionated melt increases more gradually due to the incorporation of fluorine in the structure of Ca_3SiO_5 .

4. THE ROLE OF FLUORINE IN LADLE SLAGS

The results of the study provide a perspective on the behaviour of fluorine in low-silica ladle slags. In our assessment we are guided by the following observations:

- An increase in the CaF_2 -to- SiO_2 ratio leads to the formation of CaO as primary liquidus phase, in other words, the addition of CaF_2 increases the activity of CaO in the slag. This would not be the case if F-Ca complexes were present in the melt.
- The liquidus- and main melting-temperatures, as well as the cooling behaviour are not very sensitive to the SiO_2 -to- CaF_2 ratios of the slags. This suggests that fluorine and silica are “decoupled” in the melt.
- The sequence of phases crystallising from the slags during cooling are as follows: MgO / CaO , followed by Ca_3SiO_5 and, finally, $\text{Ca}_{12}\text{Al}_{14}\text{F}_2\text{O}_{32}$. The initial sequence of phases crystallising below the liquidus (MgO / CaO followed by Ca_3SiO_5) is identical to what is found in the normalised fluorine-free system, CaO - MgO - SiO_2 - Al_2O_3 , at the 20% Al_2O_3 level. (In the fluorine-free system liquidus temperatures are of course higher - about 1800°C.)
- In terms of phase chemistry the presence of fluorine in the slag is manifested by the crystallisation of the Al-bearing phase $\text{Ca}_{12}\text{Al}_{14}\text{F}_2\text{O}_{32}$. In the fluorine-free system there are two alumina-bearing phases that crystallise near the solidus (MgAl_2O_4 – spinel and $\text{Ca}_2\text{Al}_2\text{SiO}_7$ – gehlenite) . These phases were not observed in the present study.
- Fluorine-bearing silicate phases, specifically $\text{Ca}_{10}\text{Si}_3\text{O}_{15}\text{F}_2$, which appears on the liquidus surface of the system CaO - SiO_2 - CaF_2 , were not observed. This suggests that Si-F complexes are unlikely to be present in the melt in significant proportions. A similar conclusion was reached by Schaller et al. [3].

These observations indicate that F coordinates preferentially with Al to form AlF_x complexes in the melt. This is consistent with spectroscopic studies by Schaller et al. [3] and Kohn et al.

[4], which indicate the existence of a number of Al-F complexes in fluorine-substituted silicate melts. This inference is supported by the positive correlation between the concentrations of fluorine (expressed as CaF_2) and Al_2O_3 in glass quenched from different temperatures between the liquidus and solidus (Figure 8).

The most-likely complex is AlF_6^{3-} but others such as AlF_4^- and AlF_5^{2-} have also been observed. There appears to be little chemical interaction between the silicate component of the glass matrix and the Al-F complexes and one would therefore expect a tendency for the system to unmix [3]. This is indeed observed in silica-rich melts.

The formation of Al-F complexes means that the dissolution of fluorine in the melt is associated with the formation of O^{2-} melt species. The nonbridging oxygen serves to complex high field-strength cations such as Zr and as a result the solubility of these cations tend to increase in fluorine-bearing melts. It is important to note, however, that the solubility of these cations is not directly caused by the fluorine since no metal-fluorine complexes are detected spectroscopically.

From these observations it is clear that the behaviour of fluorine in the melt will depend on the concentration of Al_2O_3 and possibly also on the concentrations of alkali metals.

5. CONCLUSIONS

The experiments provide insight into the phase chemistry of ladle fluxes. The most important observations arising from the study are the following:

- Fluorine losses occur under conditions of high humidity. The fluorine-loss problem is particularly severe in the case of laboratory-scale experiments due to the high volume-to-mass ratio of the experimental charges.
- Thermal analysis readily identifies three thermal events in fluxes containing between 3 wt% and 14 wt% CaF_2 . The main melting event, which takes place at temperatures between about 1250 °C and 1370 °C, is considered to be associated with the melting of $\text{Ca}_{12}\text{Al}_{14}\text{O}_{32}\text{F}_2$ and a large portion of the Ca_3SiO_5 . It is not the true liquidus since slags quenched from higher temperatures contain crystals of Ca_3SiO_5 , CaO, and / or MgO. The temperature of the main melting event decreases from 1346 °C to 1312 °C as the CaF_2 content of the fluxes increases from 6 to 14 wt%.
- Quench experiments indicate that the true liquidus for fluxes 2–10 is situated between 1400 °C and 1550 °C. Depending on the (CaO+ CaF_2)-to-MgO content of the slag the primary liquidus phases are CaO and MgO. The liquidus of flux 12 appears to be above 1550 °C. The relationship between liquidus temperature and CaF_2 content of the slag was not investigated in detail. The proportion monoxides that form is small and the fluidity of the slag is controlled by the main melting event.
- Very little, if any, liquid is present below about 1250 °C.
- Both MgO and CaO are present in slag containing more than 11 wt% CaF_2 , but only MgO is present in slag containing less than 11 wt% CaF_2 . Slags containing more than 11 wt%

CaF₂ would, therefore, be more compatible with doloma refractory since slags with lower CaF₂ concentrations are not saturated with CaO.

- The phase-chemical properties of the slags are consistent with the formation of Al-F complexes in the melt. That Si-F complexes are not important is consistent with our observations that the liquidus temperatures, main melting temperatures and phase-chemical properties are not sensitive to the SiO₂-to-F ratios of the slag

6. REFERENCES

- [1] Verein Deutscher Eisenhüttenleute (VDEh) Slag Atlas 2nd Edition, 1995, 616pp.
- [2] Mukerji, J., "Phase Equilibrium Diagram CaO-CaF₂-2CaO·SiO₂", Journal American Ceramic Society, 1965, 48(4), 210-213.
- [3] Schaller, T., Dingwell, D.B., Keppler, H., Knöller, W., Merwin, L. and Sebal, A. Fluorine in silicate glasses: A multinuclear nuclear magnetic resonance study. *Geochimica et Cosmochimica Acta*, 1992, 56, 701-707.
- [4] Kohn, S.C., Dupree, R., Mortuza, M.G. and Henderson, C.M.B. NMR evidence for five- and six-coordinated aluminum fluoride complexes in F-bearing aluminosilicate glasses. *American Mineralogist*, 1991, 76, 309-312.

Acknowledgements. The work was undertaken with financial support from Columbus Stainless and is published with their permission. Lengthy discussions with N. Sutcliffe and R. Nunnington contributed in no small measure to our efforts.

APPENDIX

Experimental Procedures

Preparation of Fluxes

Synthetic fluxes were prepared from oxides previously dried in muffle furnaces in air. Dried oxide mixtures were ground in an agate mortar and annealed as pellets. CaO could not be weighed accurately because it reacts with ambient air to form Ca(OH)_2 and, probably, CaCO_3 . We initially prepared an Al_2O_3 -CaO-MgO “master slag”, which was chemically homogenised through annealing at a maximum temperature of 1295 °C.

With the exception of fluxes 6a and 10a, the fluxes were prepared from appropriate mixtures of the master slag, CaF_2 , and SiO_2 . The flux mixtures were also homogenised through annealing, but for a relatively short period of time only, to minimise CaF_2 losses (initially for 45 min at 1000 °C after which time the temperature was increased to 1100 °C within 1 h, and then, finally, for 1.7 h at 1200 °C).

Thermal analysis

We used a Netzsch STA 429 and a Setaram TGDTA92 for thermal analysis of samples contained in open Pt crucibles. Runs were conducted in an argon stream. Both instruments employ type B thermocouples (Pt-30 % Rh / Pt-6 % Rh). The error in the temperature is less than 4 °C at 1064 °C and 7 °C at 1554 °C. We report uncorrected data. The maximum sample temperature was 1630 °C, and the scanning rate was varied between 2 and 10 °C/min.

We recorded DTA traces during heating and cooling at different scanning rates and extrapolated the temperatures of thermal events (onset- and peak-temperatures) to a zero scanning rate.

Thermal analysis with open Pt crucibles in argon is complex. We used a new sample for each scanning rate and recorded two or three temperature cycles at that rate. Data were excluded from further analysis when the thermal event occurred only during the first heating cycle or when there were systematic changes in the temperature of a thermal event from one cycle to the other. These data are useful providing the following considerations are taken into account.

- Samples equilibrated at temperatures below the liquidus contain more than one phase (a melt phase and one or more crystalline phases). We are interested in the thermal analysis of near-equilibrium states; e.g., we want to detect the crystallisation of phases from the melt during cooling or, alternatively, the melting of phases during heating. Thermal analysis, therefore, should be reproducible over several temperature cycles providing, of course, that the composition of the sample does not change during cycling. Thermal events that occur only during the first heating cycle, for example, are artefacts of the sample preparation procedures.
- Thermal analysis of samples with volatile components in open crucibles can be included in the analysis providing the temperature shifts of thermal events from one cycle to another are small. In the evaluation, however, one should exclude data from later cycles if they are affected by evaporation of volatile components from the sample, which would be manifested by a systematic change in the temperature at which a thermal event occurs.

Quench Experiments in Air

Pressed pellets of flux 12 were suspended in a vertical tube furnace using Pt wire and Pt loops. At the end of the experiment, samples were drop-quenched in water. Temperatures of tube furnaces used for quench experiments were measured with calibrated type B thermocouples (Pt-30 % Rh / Pt-6 % Rh). The error in the sample temperature is less than ± 10 °C including temperature fluctuations during runs.

Quench Experiments with Sealed Quartz Glass Ampoules

The flux is hygroscopic and contained water although it was stored under vacuum in a desiccator with silica gel. For experiments conducted in closed capsules, therefore, the flux had to be dried thoroughly to prevent large overpressure at high temperature. It should also be noted that water in a closed system is also likely to affect the liquidus temperature of the slag.

One end of a Pt tube (25 mm long, 4 mm diameter) was sealed with an oxygen-acetylene torch. This Pt “crucible” was filled with the flux and inserted into a quartz glass tube that was closed at one end (11 mm outer diameter, 1.5 mm wall thickness). The flux was pre-reacted for approx. 4 h at 800 °C in argon. After pre-reaction the quartz glass tube was evacuated and sealed. Through trial and error it was found that sealing had to be performed under a mild vacuum (approximately 0.25 bar) to prevent the tube from collapsing at high temperature when the quartz glass softens. Samples were drop-quenched in water. Run times varied between 11 hours and 44 hours.

Quartz glass ampoules cannot contain overpressure (or high vacuum) at high temperatures (e.g., 1450 °C). The success of the runs was gauged by the deformation of the quartz glass ampoules. In successful runs the shape and size of the ampoules did not change during reaction.

Quench Runs and Thermal Analysis with Sealed Platinum Ampoules

These experiments were performed on fluxes 6a and 10a (i.e., those mixtures where the CaF_2 was added immediately before reaction). We sealed one end of a Pt tube, which was weighed and filled with about 200 mg flux 6a or 10a (without CaF_2). It was then dried for 15 min at 1200 °C in argon. The tube was weighed again to determine the mass of Al_2O_3 - CaO - MgO - SiO_2 flux contained within. We then added the appropriate amount of CaF_2 , which had just been “dried” for 15 min at 900 °C in argon (on Pt foil). The loaded ampoule was placed in a small test tube and evacuated in an attempt to remove adsorbed humidity (10 min at ≤ 0.1 mbar). The Pt capsule was sealed *at ambient pressure* with an oxygen-acetylene torch, cooling the ampoule with a wet paper towel to minimise volatilisation of starting material. To monitor volatile losses the capsule was weighed before and after sealing and again after each TG/DTA or quench experiment (performed in argon with the ampoule suspended by a Pt wire). On average, every second Pt ampoule failed at high temperature or during quenching.

Samples for quench runs conducted below the temperature of the main melting event were homogenised for 48 h at 1450 °C. The homogenisation anneal is important because the Pt

ampoules were filled with a *heterogeneous* mixture of pre-reacted oxides (Al_2O_3 -CaO-MgO-SiO₂) and CaF₂ (the latter being loaded on top of the oxide fraction in the ampoules).

We confirmed the homogeneity of two samples of flux 6a after reacting them at 1450 °C for 20 hours and 44 hours, respectively, by analysing the glass phase by electron microprobe (80 points for the 20 hour sample and 100 points for the 44 hour sample). In both cases, the relative error of the mean cation weight fractions was less than 1 % at the 99 % confidence level. In the case of fluorine it was less than 4 % (the slightly larger error for fluorine is attributed to analytical difficulties). The relative errors are considered small, and the annealing time is sufficient for the homogenisation of the samples.

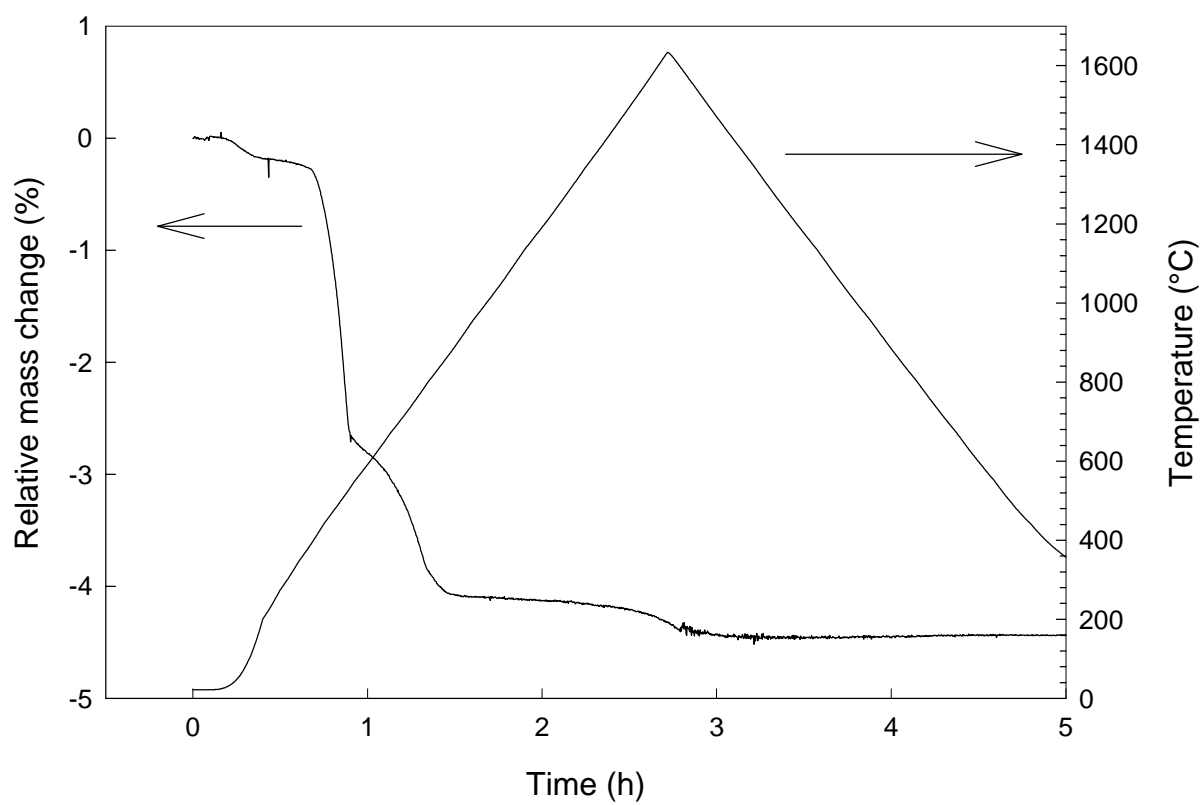


Figure 1.

Mass loss of flux 12 on heating in argon as recorded with a thermobalance. Open Pt crucible, 10 °C/min scanning rate.

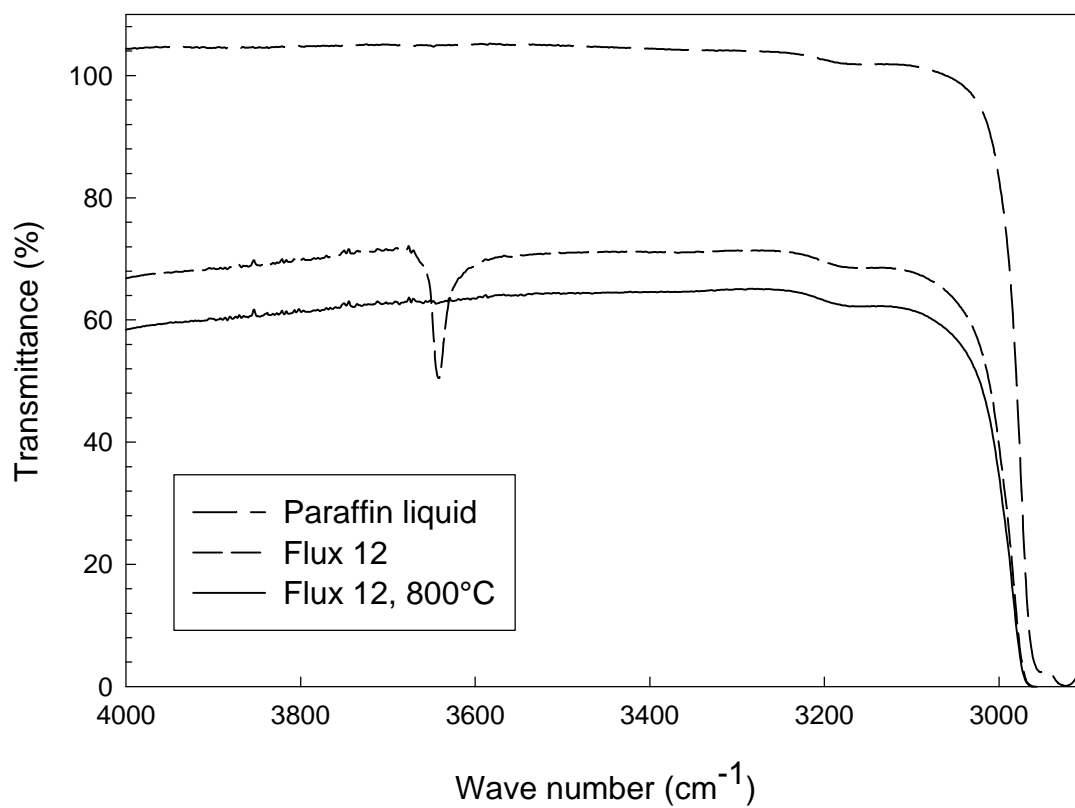


Figure 2.

Infrared spectrum of flux 12 before and after pre-reaction at 800 °C in argon. Reaction time: 10 h. The peak at 3640 cm⁻¹ is due to O-H bonds. Slag samples are suspended in paraffin liquid, the trace of which is shown for comparison.

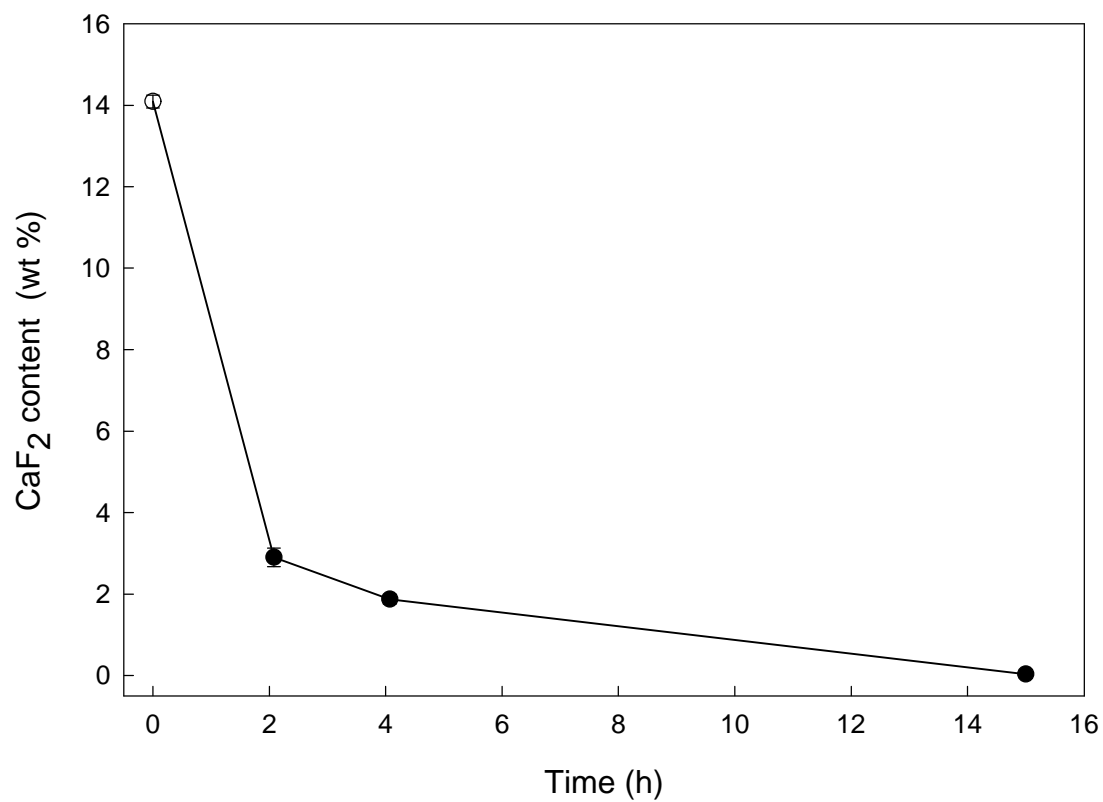


Figure 3.

Fluorine loss of flux 12 annealed in air at 1505 °C with the sample suspended in a Pt loop. Open symbol is the bulk chemical composition and solid symbols are microprobe analyses.

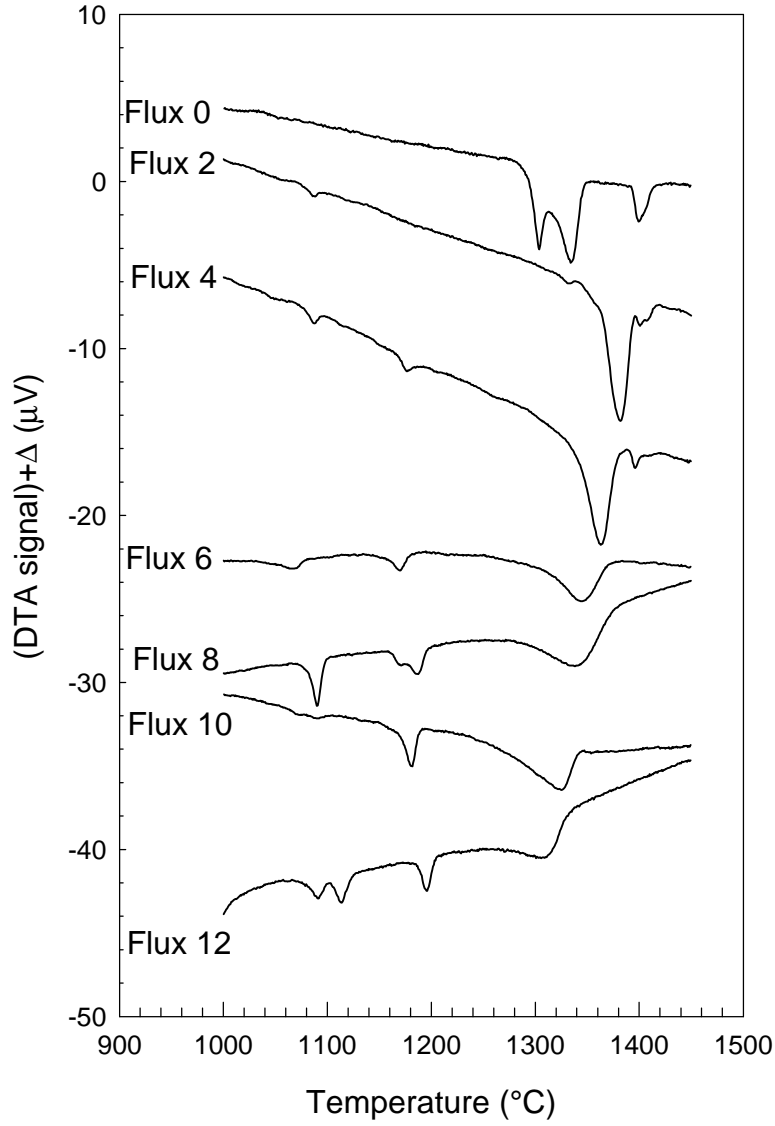


Figure 4.

DTA traces on heating at 5 °C/min. Flux 12 shows an asymmetric peak at 1312 °C that represents the main melting event. It shifts to higher temperatures as the CaF_2 content of the slag decreases. The data are scaled with m^/m_o , where m^* is 200 mg and m_o is the initial mass of the sample.*

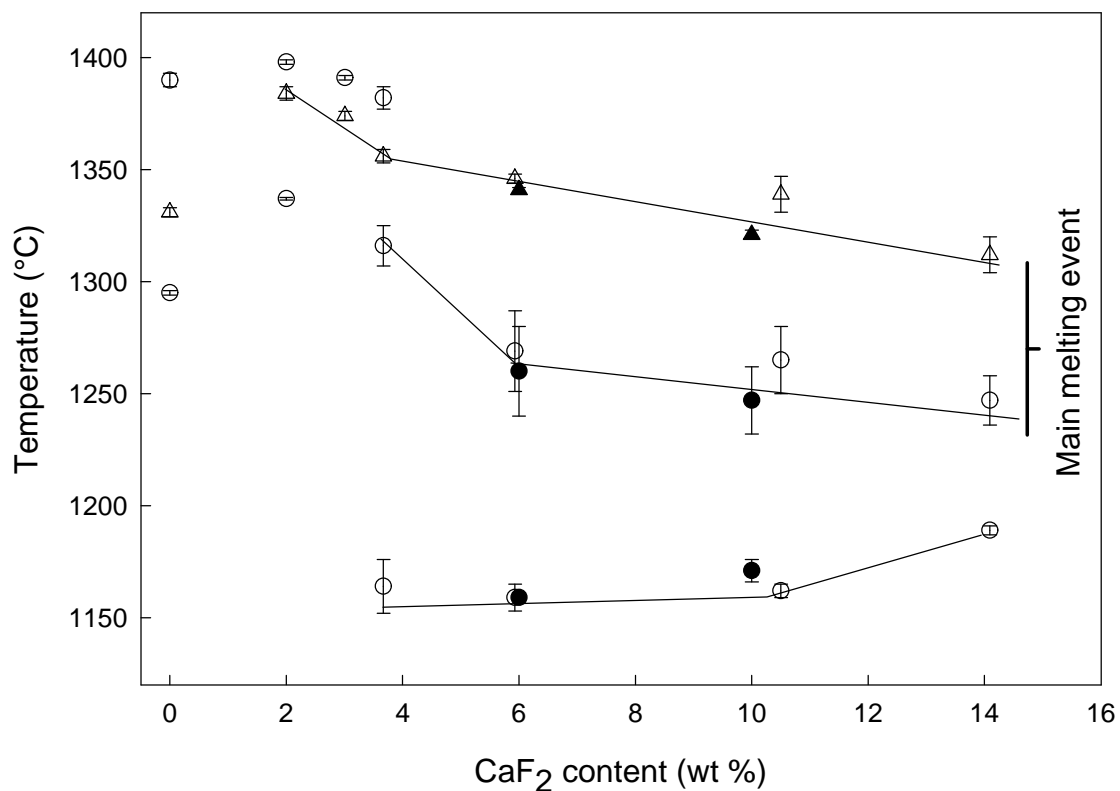


Figure 5.

Summary of thermal events on heating. Circles indicate onset temperatures; triangles, temperatures at the top of peaks. Open markers refer to runs in open Pt crucibles and closed markers to sealed Pt ampoules. The lines connect corresponding points; they do not outline fields in a phase diagram.

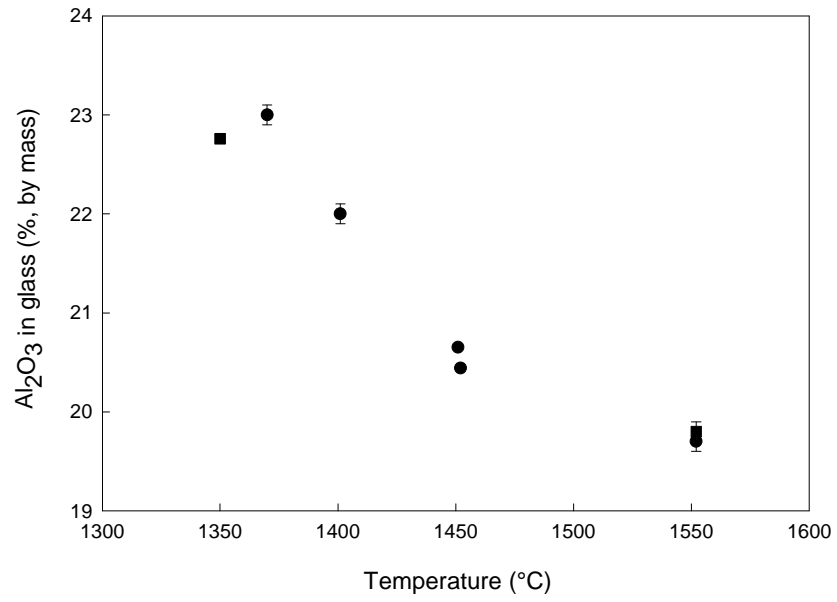


Figure 6.
Increase in the Al_2O_3 content of glass present in samples quenched from different temperatures. Circles refer to flux 6 and squares refer to flux 10. Error bars represent the uncertainties given in Table 3.

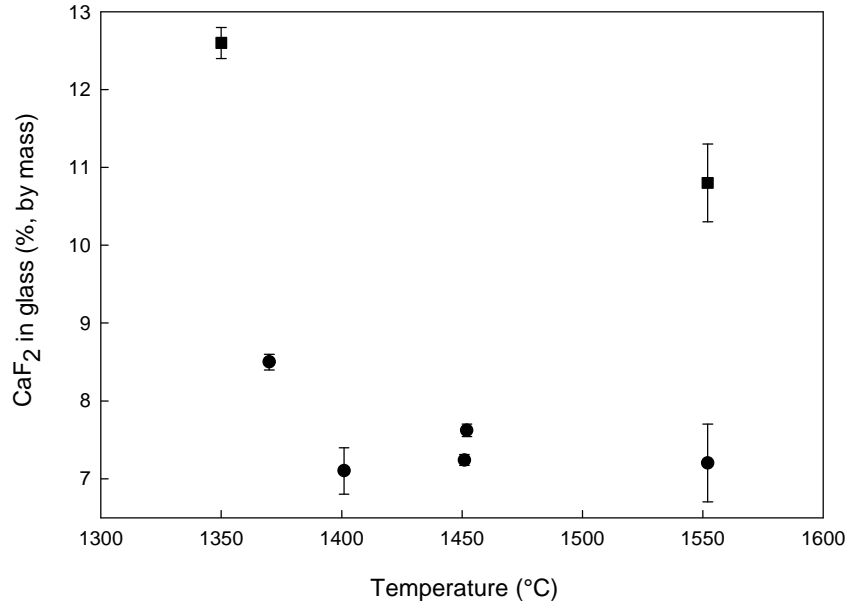


Figure 7.
Increase in the CaF₂ content of glass present in samples quenched from different temperatures. Circles refer to flux 6 and squares refer to flux 10. Error bars represent the uncertainties given in Table 3.

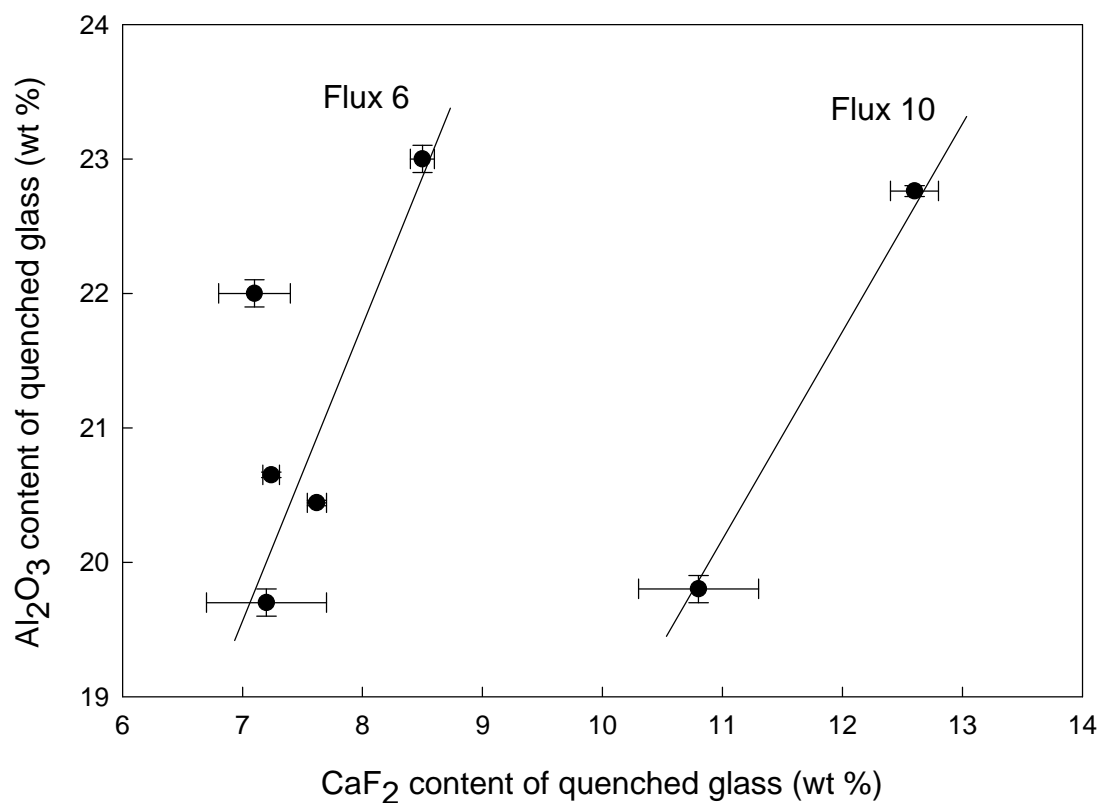


Figure 8.
Relationship between the concentrations of fluorine (expressed as CaF₂) and Al₂O₃ in glass from fluxes 6 and 10 quenched from different temperatures (data from Table 3)

Table 1.

Composition of synthetic ladle fluxes in wt%, determined by bulk chemical analysis. Weight fractions are scaled to obtain a sum of 100 wt% because the samples contained varying amounts of water. The original sum of weight fractions is given in the column labelled "Total".

	CaO	Al ₂ O ₃	MgO	SiO ₂	CaF ₂	Total
Flux 0	53.7	20.2	6.3	19.9	–	101.2
Flux 2	48.7	21.8	6.2	20.3	3.0	95.8
Flux 4	50.8	21.6	6.2	17.7	3.7	95.2
Flux 6	50.8	21.6	6.2	15.5	5.9	93.6
Flux 6	54.5	20.1	6.2	14.0	5.3	97.5
Flux 6a [*]	53.2 [#]	20.3 [#]	6.3 [#]	14.2 [#]	–	98.9
Flux 8	48.7	21.4	6.1	13.3	10.5	94.0
Flux 10	49.9	21.1	6.2	11.1	11.7	94.5
Flux 10a [*]	53.5 ^{&}	20.4 ^{&}	6.0 ^{&}	10.1 ^{&}	–	92.0
Flux 12	49.6	21.2	6.2	9.0	14.1	92.6

^{*} Before the addition of CaF₂.

[#] 94 % of scaled value to account for addition of CaF₂.

[&] 90 % of scaled value to account for addition of CaF₂.

Table 2.

Summary of phases in quenched samples (identified with X-ray diffractometry and microprobe analysis). Results from closed Pt ampoules are given in italics, other data refer to runs in quartz glass ampoules. A question mark indicates uncertainty regarding an XRD pattern.

Temp.[°C]	Flux 6 / 6a	Flux 8	Flux 10 / 10a	Flux 12
1550	glass	glass	glass, CaO?	glass, CaO
1450	<i>glass, Ca₃SiO₅ (?)</i>	—	—	—
1400	glass, MgO, Ca ₂ SiO ₄ , Ca ₃ SiO ₅ ,	glass, MgO, Ca ₃ SiO ₅	glass, CaO, MgO?	glass, CaO, MgO?, Ca ₂ SiO ₄
1350–70	<i>glass, MgO, Ca₃SiO₅</i>	—	<i>glass, CaO, MgO, Ca₃SiO₅</i>	—
1250	—	—	CaO, Ca ₃ SiO ₅ , Ca ₁₂ Al ₁₄ F ₂ O ₃₂ , MgO	CaO, MgO?, Ca ₃ SiO ₅ , Ca ₁₂ Al ₁₄ F ₂ O ₃₂
1225	<i>MgO, Ca₃SiO₅, Ca₁₂Al₁₄F₂O₃₂</i>	—	<i>CaO, MgO, Ca₃SiO₅, Ca₁₂Al₁₄F₂O₃₂</i>	—

Table 3.
Electron microprobe analyses of glass present in the quenched slag samples.

Temp. (°C)	CaO	Al ₂ O ₃	MgO	SiO ₂	CaF ₂	Total
Flux 6 / 6a						
1552	52.8(4)	19.7(1)	6.56(4)	14.33(8)	7.2(5)	100.5(3)
1452	50.63(7)	20.44(2)	5.774(9)	13.14(2)	7.62(8)	97.60(5)
1451	52.06(6)	20.65(2)	5.85(1)	13.54(1)	7.24(7)	99.33(7)
1401	52.2(3)	22.0(1)	5.29(7)	13.42(8)	7.1(3)	100.1(3)
1370	51.1(2)	23.0(1)	5.00(3)	12.7(1)	8.5(1)	100.2(1)
Flux 8						
1553	53.4(3)	19.44(6)	6.54(8)	12.48(7)	8.9(4)	100.8(3)
Flux 10						
1552	51.9(3)	19.8(1)	6.60(5)	10.44(3)	10.8(5)	99.5(3)
1350	50.5(2)	22.76(4)	4.27(2)	9.78(4)	12.6(2)	99.9(1)
Flux 12						
1554	51.3(4)	20.52(7)	6.66(3)	8.72(2)	13.7(4)	101.0(2)